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INCINERATING THE PESTICIDE ETHYLENE DIBROMIDE (EDB) --- A FIELD-SCALE TRIAL BURN EVALUATION OF ENVIRONMENTAL PERFORMANCE

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16. ABSTRACT

This paper is an overview of the trial burn of a representative quantity of waste EDB pesticides and is based upon results presented in the Final Report prepared for Rollins by Alliance Technologies Corporation. The results demonstrated that this brominated material could be safely incinerated with no significant bromine stack emissions. Recent experience by industry with brominated wastes strongly suggested that the major objection to incinerating EDB, the uncontrolled release of bromine (Br) to the atmosphee, could be overcome by the addition of sulfur to the combustion process. One of the major objectives of this trial burn was to verify that the presence of sulfur as SO_2 would force the conversion reaction of Br to hydrogen bromide (HBr).

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I. OVERVIEW

An alternative method for disposal of cancelled liquid pesticide ethylene dibromide (EDB) was evaluated in a field-scale incinerator trial burn in December 1987. The trial burn was conducted at Rollins Environmental Services, Inc. (RES(TX)), a major, permitted PCB and RCRA commercial incineration facility. Previously, EPA did not view incineration as a viable destruction process for the large volume (nearly 300,000 gallons) of the bromine-laden EDB it had stockpiled. However, recent experience by industry with brominated wastes strongly suggested that the major objection to incinerating EDB, the uncontrolled release of bromine (Br) to the atmosphere, could be overcome by the addition of sulfur to the combustion process. One of the major objectives of this trial burn was to verify that the presence of sulfur as SO_2 would force the conversion reaction of Br to hydrogen bromide (HBr). Hydrogen bromide can be readily scrubbed and is, therefore controllable within the incineration system. There were four objectives for the test burn program:

1. To confirm the ability of the incinerator to achieve the levels of destruction and removal efficiency (DRE) for the principal organic hazardous constituents (POHCs) of the EDB materials as required under RCRA.

2. To verify the effectiveness of sulfur addition to the combustion process to force the formation of HBr, and thus control bromine releases from the stack by removing the easily scrubbed HBr in the wet scrubbing system.

3. To assess the compatibility of co-firing EDB with typical waste streams incinerated at the facility.

4. To attempt to demonstrate a mass balance on bromine for the incineration process as a further assessment of overall performance.

This paper is an overview of the trial burn of a representative quantity of waste EDB pesticides and is based upon results presented in the Final Report prepared for Rollins by Alliance Technologies Corporation. The results demonstrated that this brominated material could be safely incinerated with no significant bromine stack emissions. In addition, high destruction efficiencies of the pesticides' POHCs were achieved. In response to these

conclusions, EPA has since approved incineration of approximately two-thirds of the EDB liquid pesticide stocks and a smaller quantity of miscellaneous wastes and anticipates completing incineration of all EDB stocks requiring disposal by Fall.

II. FACILITY DESCRIPTION

The commercial hazardous waste incinerator (Train I shown in Figure 1) operated by RES(TX) at its Deer Park, Texas facility is designed to thermally oxidize and destroy liquid, solid and gaseous hazardous wastes. This unit is capable of operating at combustion temperatures in excess of 2,000°F with a hot gas retention time of over 2 seconds and a combustion efficiency of greater than 99.9 percent. All combustion gases are quenched, cooled, and scrubbed by a system consisting of a saturator, packed tower condensers, and a high energy Venturi scrubber.

This unit is unique in that it has two separate combustion chambers feeding a common afterburner. The first chamber is a rotary kiln capable of burning waste liquids, gases, sludges, and solids. The second is a Loddby liquids burner which feeds tangentially into the afterburner. The liquid waste injection burners in each chamber are equipped with natural gas ignitors and supplemental gas burner guns for the purpose of initial refractory heat-up, flame stability, and supplemental heat.

The combustion gases from the aforementioned burners combine in the afterburner with a horizontal cyclonic effect to achieve adequate mixing turbulence. From here, the hot gases pass through a refractory-lined cylindrical duct (the "hot duct") and discharge into a water-quenched saturator followed by dual-packed tower condensers, and finally through a high energy impact-type Venturi scrubber. Before exiting via the stack, the gas passes through a mist eliminator to remove entrained water droplets.

Two induced draft fans in series provide the energy for the scrubber, serve to superheat much of the remaining stack gas moisture content, and maintain the entire incinerator at a negative pressure sufficient to prevent fugitive emissions. Upon leaving the fans, the gases pass upward through a 100-foot tall stack and exit into the atmosphere. The stack emissions are normally quite low in opacity due to low particulate levels and the invisible "dry steam" condition of any residual moisture.

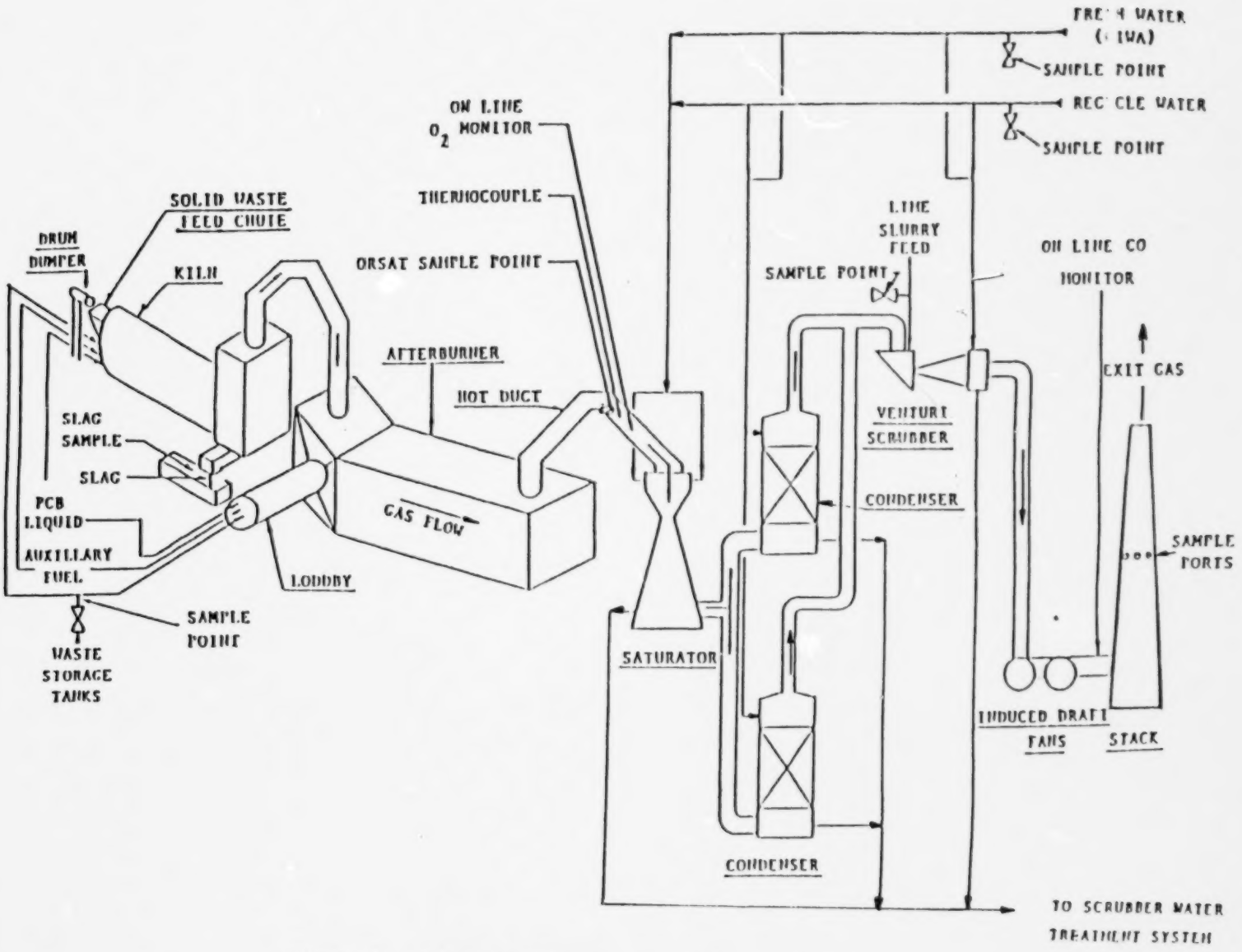

Figure 1. Schematic diagram of RES(TX) incinerator.

Scrubber water from the saturator, condensers, and Venturi is neutralized using alkaline material. The suspended solids are removed from the scrubber water with a filter cake-producing screening device. The water is cooled in a cooling tower and recycled to the scrubber system. A portion of the cooled water is discharged through a National Pollutant Discharge Elimination System (NPDES) outfall to prevent buildup of excess salts. This outfall discharges to Tucker Bayou, and then to the Houston Ship Channel. A generalized schematic diagram of the incinerator's scrubber water treatment system is provided in Figure 2.

III. METHODS

The pesticide shipped to the Rollins site for the Trial Burn testing program was comprised of nearly 20,000 gallons of an EDB/ethylene dichloride (EDC)/carbon tetrachloride (CCl_4) mixture and another 5,000 gallons of an EDB/chloropicrin formulation. During the test program, pesticide feed rates represented 10 to 15 percent of the facility's 300 lb/min net waste throughput capacity. Scoping tests, which were brief test firings of the EDB pesticides, were included as the initial part of the trial burn program to determine any immediate or observable performance impacts. These scoping runs were also used to select appropriate waste feed rates to be used in the more detailed trail burn portion of the evaluation. Although scoping operations showed good performance with various combinations of the two types of formulations, the trial burn itself was done with the non-chloropicrin material to ensure that accurate destruction results would be obtained on the more difficult to incinerate constituents.

Approximately 21,400 gallons of material (of the 25,000 gallons) remained after completion of the scoping and trial burn program. This remaining material was incinerated at Rollins following the trial burn, further demonstrating that the pesticide caused no apparent problems during materials handling and incineration. There were no discernible problems, corrosion or malfunctions, as the remaining 21,400 gallons of material were destroyed. The pesticide test materials for the burn were supplied from inventories of EDB stored in Liberty, Missouri, and Ashburn, Georgia.

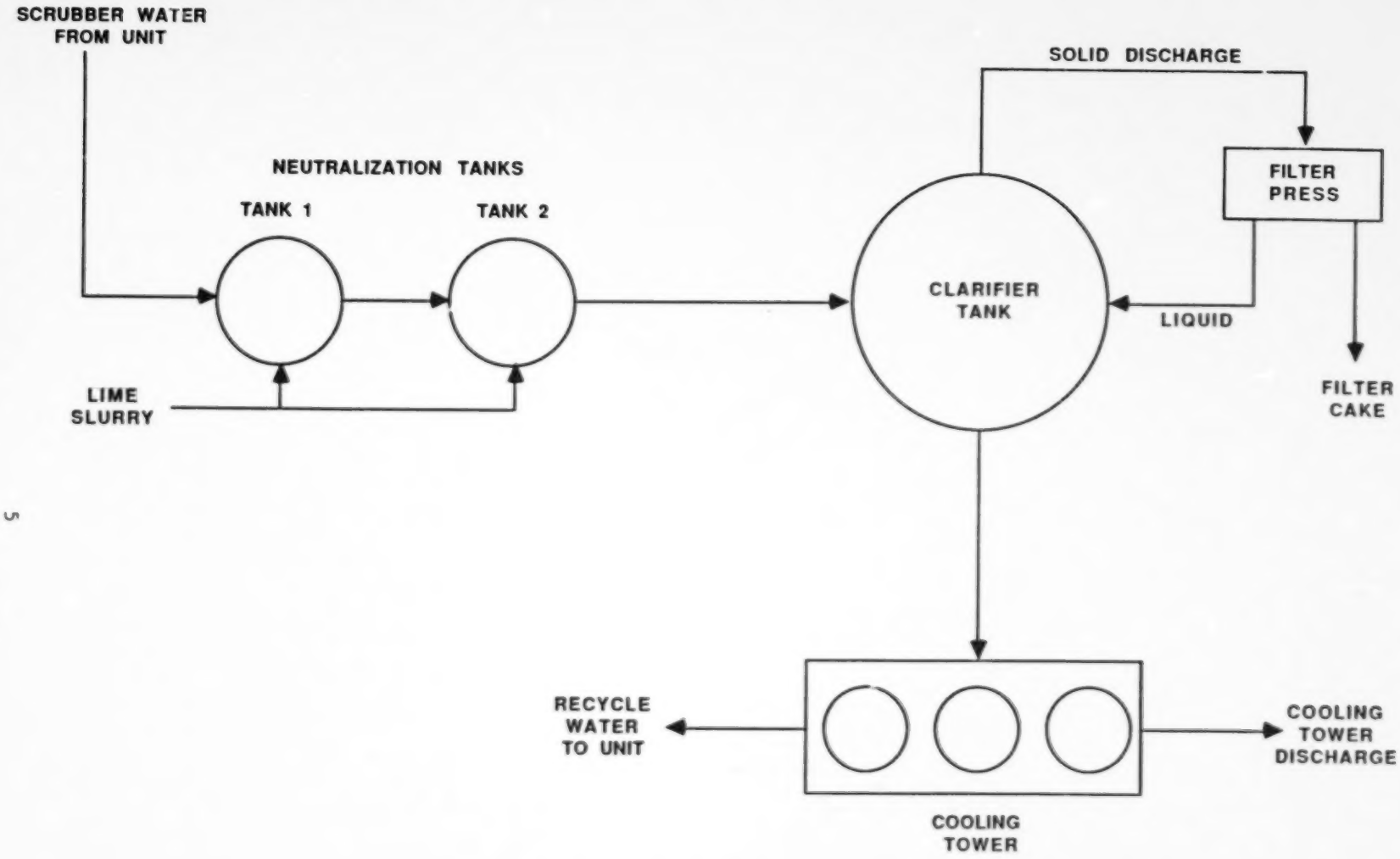

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Figure 2. Scrubber water treatment and recycle system.

RES(TX) contracted with Alliance Technologies Corporation of Bedford, Massachusetts, to prepare a Quality Assurance Plan, to conduct all field sampling and laboratory analyses, and to report data. Grab samples of all waste feed, process water, and residual streams were collected every 30 minutes during each 2-hour run, and composited on a per run basis. These streams included cooling water discharged from the cooling tower, fresh water supplied by the Coastal Industrial Water Authority (CIWA), lime slurry fed to the neutralizing system, ash discharged from the rotary kiln, and filter cake discharged from the scrubber water treatment system. Samples of incinerator off-gases were collected from the hot duct prior to the scrubber system and from the stack prior to discharge to atmosphere.

At the hot duct location, bromine/chlorine compounds were sampled with a midget impinger train employing two impingers with acidified DI water (for collection of Br_2/Cl_2), two impingers with 0.1N NaOH (for collection of HBr/HCl), and one impinger with silica gel for moisture removal. Sulfur oxides were sampled with a similar midget impinger train operated in conformance with EPA Method 6. Integrated gas samples were also collected in Tedlar bags for determination of O_2 and CO_2 content by Orsat analysis.

Flue gas sampling was conducted at the stack location approximately 59 feet above ground level where the inside diameter is 6 feet. The sample ports were located 41 feet upstream of the discharge point and 35 feet downstream of an expansion point in the stack. Flue gas sampling was conducted to determine emission rates and/or concentrations of the following parameters: particulate matter; metals (antimony, arsenic, beryllium, cadmium, chromium, copper, iron, lead, mercury, nickel, selenium, silver, thallium, vanadium, and zinc); total bromine and chlorine including HBr and HCl; volatile compounds including the three POHCs - EDB, EDC, and CCl_4; bulk gases (O_2 and CO_2); and pollutant gases (CO, NO_x, and SO_2). Sampling for particulate matter and metals was conducted using EPA Reference Methods 1-5, with modifications to the impinger solutions to allow quantification of the metals of interest.

Sampling for bromine and chlorine at the stack location was conducted with an identical sampling train and at the same time as was done in the hot duct. Stack gas concentrations of the three POHCs (EDB, EDC, and CCl_4) and other volatile organics were measured with the volatile organic sampling train

(VOST) in accordance with procedures specified in Method 0030 of SW-846, 3rd. Edition. Continuous monitoring for bulk gases (O_2 and CO_2) and pollutant gases (CO, SO_2, and NO_x) was performed in accordance with EPA Reference Methods 3A (O_2 and CO_2), 6C (SO_2), 7E (NO_x), and 10 (CO), as well as procedures specified in EPA publications 340/1-83-016 regarding setup and operation.

IV. RESULTS

Table 1 summarizes test conditions during the triplicate run test program. It should also be noted apart from Table 1 that during scoping tests, the non-chloropicrin EDB material (with its 9 to 12 percent EDB content) was test-fired at up to 50 lb/min. EDB/chloropicrin material (38 to 40 percent EDB) was individually tested at up to 40 lb/min. Both formulations were also co-fired satisfactorily at a combined feed rate of approximately 90 lb/min. Table 2 summarizes the performance results from the overall test program.

During the EDB trial burn, the incinerator achieved excellent destruction and removal efficiencies for each POHC. The RCRA DRE standard is 99.99 percent and in each case, the DRE exceeded 99.9999 percent. Particulate emissions were 0.0081 to 0.023 gr/dscf (corrected to 7 percent O_2). These values are well below the RCRA emission limit of 0.08 gr/dscf (corrected to 7 percent O_2).

The results showed that no bromine (Br_2) was detected in stack emissions (detection limit of 5 mg/dscf), and that small amounts (0.007 to 0.188 lb/hour) of bromide (as HBr) were emitted. This indicated that virtually all of the bromine compounds in the waste were converted to bromide in the combustion chamber and were subsequently removed from the combustion gases by the scrubber. Scrubber removal efficiency for bromide ranged from 99.94 to 99.98 percent. The bromide formation reaction was effected by the addition of sulfur to the combustion chamber in the form of dilute sulfuric acid (H_2SO_4). The stack opacity maintained low levels (less than 5 percent) while the sulfur was being fed. During the scoping runs, the sulfur stream was intentionally stopped several times for brief periods (each stoppage lasted only a few seconds). A visible brownish plume resembling typical

TABLE 1. INCINERATOR OPERATING CONDITIONS FOR EDB TEST BURN PROGRAM

	Run No. 1		Run No. 2		Run No. 3		Averages	
	Parameters	Feed Rate (lb/min)	Parameters	Feed Rate (lb/min)	Parameters	Feed Rate (lb/min)	Parameters	Feed Rate (lb/min)
Run Date	12-11-87		12-11-87		12-11-87			
Run Time, Start/Stop	11:32/13:38		15:30/17:35		18:04/20:10			
Waste Feed Material and Location (a)	A-Kiln	50.3	A-Kiln	48.9	A-Kiln	50.8	A-Kiln	50.0
	C-Kiln	50.1	C-Kiln	16.6	C-Kiln	14.0	C-Kiln	26.9
	D-Loddby	86.0	D-Loddby	51.0	D-Loddby	52.6	D-Loddby	63.2
	E-Aftrbrn	16.2	E-Aftrbrn	0.7	E-Aftrbrn	0.4	E-Aftrbrn	5.8
	F-Kiln	65.3	F-Kiln	65.9	F-Kiln	66.4	F-Kiln	65.9
	H-Kiln	3.7	H-Kiln	4.0	H-Kiln	0.0	H-Kiln	2.6
	I-Kiln	16.4	I-Kiln	7.8	I-Kiln	5.6	I-Kiln	9.9
	Total	288.0	Total	194.9	Total	189.8	Total	224.2
Kiln Exit Gas Temperature, F	1707		1862		1810			1793
Afterburner Temperature, F	2381		2275		2289			2315
Hot Duct Temperature, F	2209		2209		2236			2218
Hot Duct Flowrate, dscfm	36,039		38,499		37,533			37,357
Stack Temperature, F	148		146		146			147
Stack Flowrate, dscfm	39,787		43,026		42,601			41,805
Scrubber Water Flowrate, gpm	403		403		405			404
Lime Flowrate to Scrubber, lb/min	137		21		21			60
Cooling Tower Discharge Flow, gpm	328		386		341			352
Scrubber Water Recycle Rate, gpm	5236		5261		5262			5253

(a)
A = EDB Waste Liquid
C = Industrial Waste Liquid
D = PCB Waste Liquid
E = T-Ox Wastewater
F = PCB Solids
H = Glass (Kiln Conditioner)
I = Sulfuric Acid (10% w/w)

TABLE 2. EDB TEST BURN PROGRAM SUMMARY

Run No.	1	2	3	AVG
POHCs - DRE - %				
CCl4	> 99.9999	> 99.9999	> 99.9999	> 99.9999
EDB	> 99.9999	> 99.9999	> 99.9999	> 99.9999
EDC	> 99.9999	> 99.9999	> 99.9999	> 99.9999
Particulate Emissions				
gr/dscf @ 7% O2	0.0112	0.0092	0.0078	0.0094
emission rate, lb/hr	3.0015	2.5517	2.1285	2.5606
percent opacity	< 5	< 5	N/A	< 5
Metals Emissions, lb/hr				
Antimony	0.0000	0.0000	0.0000	0.0000
Arsenic	0.0000	0.0000	0.0000	0.0000
Beryllium	0.0004	0.0004	0.0004	0.0004
Cadmium	0.0005	0.0005	0.0006	0.0005
Chromium	0.0157	0.0074	0.0032	0.0088
Copper	0.1311	0.0897	0.1205	0.1138
Iron	0.1320	0.1013	0.1081	0.1138
Lead	0.0910	0.0532	0.1134	0.0859
Mercury	0.0002	0.0002	0.0002	0.0002
Nickel	0.0116	0.0089	0.0131	0.0112
Selenium	0.0000	0.0000	0.0000	0.0000
Silver	0.0002	0.0004	0.0004	0.0003
Thallium	0.0000	0.0000	0.0000	0.0000
Vanadium	0.0006	0.0007	0.0007	0.0007
Zinc	0.2953	0.0783	0.1382	0.1706
Acid Gas Emissions, lb/hr				
HBr	0.188	0.083	0.067	0.113
HCl	0.214	0.21	0.175	0.200
Br2	0.000	0.000	0.000	0.000
Cl2	0.150	0.139	0.000	0.096
Gas Concentration Data				
O2, %	10.0	10.3	10.3	10.2
CO2, %	8.8	8.1	8.0	8.3
CO, ppm	19.2	15.7	15.8	16.9
NOx, ppm	62.8	53.1	47.0	54.3
SO2, ppm	45.8	44.5	42.2	44.2
Pollutant Gas Emission Rates, lb/hr				
CO	3.32	2.91	2.87	3.03
NOx	17.85	16.14	14.04	16.01
SO2	18.1	18.83	17.54	18.16
Incinerator Combustion Efficiency, %	99.98	99.98	99.98	99.98
Scrubber Efficiency, %				
HBr/Br2	99.94	99.97	99.98	99.96
HCl/Cl2	99.99	99.98	99.99	99.99
SO2	77.68	66.03	60.46	69.89
Total Bromine Mass Balance				
Output/Input, % (log fit)				85
Output/Input, % (linear fit)				105

bromine fumes did emit from the stack whenever the sulfur stream was stopped. Those momentary emissions, coupled with the reliable lack of visible emissions with the sulfur present, demonstrated the effectiveness of sulfur to promote the reaction in which Br_2 is converted to HBr. During the trial burn and subsequent analysis of samples, confidence in the sulfur reaction was further confirmed by stack bromine levels which did not exceed the detection limit.

One objective of the trial burn was to attempt a short-term mass balance for bromide across the incineration system. This determination was complicated by several issues:

- Because of the large inventory of scrubber water (>1 million gal), the system has an inherent lag time such that samples collected at the cooling tower discharge were not representative of steady-state conditions;
- The incinerator was feeding both EDB and substantial amounts of other waste feed streams during the sampling runs and these streams had to be checked for any bromine content; and
- The scrubber system recycles approximately 5,250 gpm of water back to the system and discharges about 350 gpm to the outfall.

The following calculations were performed in order to account for the above issues. First, the lag time (or scrubber system water residence time) was calculated based on the total volume of the overall scrubber system (>1 million gal) and the known discharge and recycle water flow rates. The water residence time was thus approximated at 3.25 hours. Because of this residence time, each of the bromide concentrations measured at given times in the cooling tower discharge over the course of each run were assumed to be indicative of what was occurring in the scrubber system 3.25 hours earlier. To account for this, the actual measured bromide concentrations of the composite samples for a given run were paired with the midpoint times of each run (corrected for the residence time), and linear and log fit regression equations were computed for the three data points. The concentrations for the actual run times were then computed from these regression equations (start, middle, and end of each run). The difference in concentration over each run from beginning to end was then computed as was the concentration difference

between runs. In addition, a concentration difference was determined over the duration of the entire trial burn period (from the beginning of Run 1 to the end of Run 3) since EDB waste continued to be fired in the unit between runs.

V. CONCLUSIONS

The results from the EDB scoping and test burn program, conducted during the week of December 7, 1987 at RES(TX), demonstrated that incineration of these bromine-laden pesticide wastes is an effective disposal method. Both DRE and emissions levels were consistently within RCRA performance standards. There were no discernible operational problems or differences in overall incinerator performance noted during the scoping and trial burn periods as pesticide waste feed was added to the unit's normal range of various PCB and RCRA materials. The success of a subsequent 21,400 gallon operational burn period which followed the scoping and trial burn further supported our conclusion that these pesticides could be destroyed safely by incineration.

As mentioned in the Overview, EPA then proceeded with incineration of the remaining EDB inventories to be disposed of on a routine basis. At this juncture, the contents of about two-thirds of the rail cars, nominally 15,000 to 18,000 gallons each, plus a lesser amount of product-containing containers, have been incinerated. The overall disposal task is scheduled to be completed this Fall.